RESEARCH ARTICLE

Statistical mechanics of hard spheres: the scaled particle theory of the hard sphere fluid revisited

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Abstract: The aim of this paper is to exhaust the possibilities offered by the scaled particle theory as far as possible and to confirm the reliability of the virial coefficients found in the literature, especially the estimated ones: B i for i > 11. In a previous article (J.Math.Phys.36,201,1995) a theoretical equation of state for the hard sphere fluid was derived making use of the ideas of the so called scaled particle theory which has been developed by Reiss *et al*.(J.Chem.Phys.31,369,1959). It contains two parameters which could be calculated. The equation of state agrees with the simulation data up to high densities, where the fluid is metastable. The derivation was besed on a generalized series expansion. The virial coefficients B 2 , B 3 and B 4 are exactly reproduced and B 5 , B 6 and B 7 to within small deviations, but the higher ones up to B 18 are systematically and significantly smaller than the values found in the literature. The scaled particle theory yields a number of equations of which only four were used. In this paper we make use of seven equations to calculate the compressibility factors of the fluid. They agree with the simulation data slightly better than those yielded by the old equation. Moreover, the differences between the calculated virial coefficients B i and those found in the literature up to B 18 are very small (less than 4 percent).

Keywords: Hard sphere fluid; scaled particle theory; contact cor; relation function; series expansion; compressibility factors; virial co; efficients

1 Introduction

Suppose that a theoretical physicist has to deal with a series expansion and that it is impossible to prove mathematically that it converges. If this series yields a physically meaningful result, then it must converge.

Arnold Sommerfeld

In[1] a new theortical equation of state for the hard sphere fluid was found.Its derivation is based on the ideas of Reiss *et al*. in [2]. In that theory one considers an empty spherical region of radius r in the fluid, which we shall call a hole. In the following the particle diameter σ is taken as a unit of length. As a measure of the particle density we use the packing fraction $y = N\pi\sigma^3/6V$; the compressibility factor is denoted by $Q = pV/NkT$. One of the main concepts of the scaled particle theory is the contact correlation function G(y,r) which is defined in the following manner: if the hole of radius r is bounded by a thin shell of thickness dr, then $4\pi r^2 \rho G(y,r)dr(\rho - N/V)$ is the conditional probability that the shell is occupied by at least one particle center(the condition is that the hole is empty). From this follows that $\rho G(y,r)$ is the average density of particle centers just outside the hole[2]. Reiss *et al*. have shown that $G(y,\infty) = Q(y)$. To derive their equation of state they used a series expansion of G(y,r) in powers of 1/r. In [1], we

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have replaced that expansion by a more general one, namely

$$G(y,r)+\sum_{i=1}^{k}A_i(y)t_i(r) \quad \text{if} \quad r>\frac{1}{2} \tag{1}$$

where $t_i(r)$ forms a set of linearly independent functions with the property $\lim_{r\to\infty} t_i(r) = 0$. It was tacitly assumed that they form a complete set. Truncating the series after the third term, we found the following Pad´e-like expression for the compressibility factor of the system

$$Q(y)=\frac{1+q_1y+q_2y_2}{(1-y)^2(1+(q_1-2)y)} \tag{2}$$

Here q_1 and q_2 are parameters which depend on the functions $t_1(r)$ and $t_2(r)$. With the help of the low density expansion of the radial distribution function of the fluid we calculated these functions and obtained

$$q_1 = 1.2117...\text{and}q_2 = 1.4234...$$

With these values of the parameters, equation (2) reproduces the known virial coefficients and the simulation data of the fluid significantly better than the Reiss equation, which has the same form as (2) but different values of q_1 and q_2, namely $q_1 = q_2 = 1$.

2 The basic relations of the scaled particle theory

In this section a brief summary of the theory of Reiss *et al.* will be given. These authors have shown that the contact correlation function G(y, r) of a one component fluid system of hard spheres fulfills the following exact relations[2]

$$G(y,\infty) = Q(y) \tag{3}$$

$$Q(y) = 1 + 4yG_1(y)\text{with } G_1(y) \equiv G(y, 1) \tag{4}$$

$$G_2(y)=G(y,\frac{1}{2})=\frac{1}{1-y} \tag{5}$$

$$G_3(y)\equiv G'\left(y,\frac{1}{2}\right)=\frac{6y}{(1-y)^2} \tag{6}$$

$$G_4(y)\equiv G''(y,\frac{1}{2})=12\frac{1+5y^2}{(1-y)^3}-\frac{12Q(y)}{1-y} \tag{7}$$

Here

$$G'(y,\frac{1}{2})=\left(\frac{\partial G(y,r)}{\partial r}\right)r=1/2 \quad \text{and} \quad G''\left(y,\frac{1}{2}\right)=\left(\frac{\partial^2 G(y,r)}{\partial r^2}\right)r=1/2 \tag{8}$$

The derivatives in (15) are taken to the right of r = 1/2[2]. We remark that (4) follows from

$$G(y,1) = g(1)$$

where g(1) is the contact value of the radial distribution function $g(r)$ which depends on the density. An exact relation between G(y,r) and $g(r)$ is only known for r = 1 and r–> ∞. Further relations can be derived; they contain the functions $\partial g(r)/\partial r)_{r=1} = g(1)$, $(\partial^2 g(r)/\partial r^2)_{r=1}$,... of y, of which, from our knowledge, no exact information is available. One of these relations is

$$G_5(y)\equiv G'''\left(y,\frac{1}{2}\right)=\frac{48y\left(1+16y+10y^2\right)}{(1-y)^4}+\frac{288y(1-5y)}{(1-y)^2}g(1)-\frac{96y}{1-y}g'(1) \tag{9}$$

In the following we shall make use of approximate theoretical values of the function $g(r)$, obtained by Heying and Corty[3] for $0.3 \le \rho \le 0.9$ or $0.157 \le y \le 0.471$. These values could be smoothed by means of

$$g'(1)=-y.\exp(1.61388+3.59223y+5.30448y^2) \tag{10}$$

Furthermore, Q(y) and G(y, r) are related by the so called thermodynamic condition. This is a another basic relation [2]

which is a consequence of $N\mu = F + pV$ where F denotes the Helmholtz free energy and μ the chemical potential.

3 The thermodynamic condition

We denote the Helmholtz free energy of the system by F and define $\phi(y) = F / NkT$. $\phi(y)$ is thus the free energy per particle in units of kT . The chemical potential μ can be decomposed as follows[2] (β = 1/kT):

$$\beta\mu = \beta\mu_0 + W(1)$$

Here W (1) is the reversible work needed to create a hole of radius r = σ in the hard sphere system (r/σ = 1). To determine μ0, we take the limit σ → 0 so that the interactions between the particles are switched off and that W (1) = 0. Then we have that [4]

$$\phi(y) = \ln \frac{\mu V}{N} - 1$$

from which follows that

$$\beta\mu_0 = \ln \rho$$

If the interactions are switched on again we have that [2]

$$W(1) = 4\pi\rho \int_1^\infty G(y,r) r^2 dr$$

From N μ = F + pV follows that βμ = ∅ (y) + Q(y) so that

$$\phi(y) + Q(y) = \ln\rho - \ln(1-y) + 24y \int_{1/2}^1 G(y,r) r^2 dr \tag{11}$$

Here use was made of the fact that G(y,r) = 1/(1−8r³y) for r/σ < 1/2 [2]. We call the exact relation (11) the thermodynamic condition.

4 A more general expansion of G(y, r)

In [4] and [5] the series expansion (1) was generalized as follows:

$$G(y,r) = Q(y)u(r) + A_0(y)u_0(r) + \sum_{i=1}^{k} A_i(y)t_i(r) \quad \text{if} \quad r > \frac{1}{2} \tag{12}$$

where

$$A_0(y) = \ln(1 - my)/y$$

Here 1/m is the density at which the compressibility factor of a frozen system diverges. We now suppose that in the case of the fluid 1/m is larger than the density of close packing $\pi\sqrt{2}/6$ and thus has no physical significance. Therefore the term $A_0(y)$ will be dropped. We thus replace (12) by

$$G(y,r) = Q(y)u(r) + \sum_{i=1}^{k} A_i(y)t_i(r) \quad \text{if} \quad r > \frac{1}{2} \tag{13}$$

This series differs from (1) only by the appearence of the function u(r) and we assume that the $A_i(y)$ have no physical pole. It is again supposed that $t_i(r)$ form a complete set. To fulfill (3), we require that $\lim_{r\to\infty} t_i(r) = 0$ for i = 0, ..., n and that $\lim_{r\to\infty} u(r) = 1$.

We remark that (13) can also be written as follows:

$$G(y,r) = \sum_{i=1}^{k+1} A_i(y)t_i(r) \quad \text{if} \quad r > \frac{1}{2}$$

where $A_{k+1}(y) = Q(y)$ and $t_{k+1}(r) = u(r)$.

5 A differential equation

We truncate the series (13) after the k th term and follow the same reasoning as in [4]. We find that (13) leads to

$$\phi(y) = \ln\rho - \ln(1-y) + (\beta y - 1)Q(y) + y\sum_{i=1}^{k} a_i Gi(y) \tag{14}$$

Here α_i and β are parameters which will be determined.

The equations which appear in the following are partly derived by means of mathematical computer software. Therefore some details - which we consider to be superfluous- were omitted.

Equation (14) can be written as

$$f_2(y)y\frac{d\phi(y)}{dy}-\phi(y)+f_1(y)=0 \tag{15}$$

If k = 4 $f_1(y)$ and $f_2(y)$ are of the form

$$f_2(y)y\frac{d\phi(y)}{dy}-\phi(y)+f_1(y)=0 \tag{16}$$

and

$$f_2(y)=\frac{b_1+b_2y+b_3y^2}{1-y} \tag{17}$$

The coefficients a_i ad b_i depend on the five parameters α_i and β.

If k = 5 a similar differential equation can be found. In this case we have six parameters α_i and β. The functions $f_i(y)$ are now more complicated than those in (16) and (17) but there is no need to give their explicit expressions here.

6 Approximate solution of the differential equation

As it is not clear how an analytical solution of (15) could be found, we search for an approximate solution. To find the latter, we proceed as follows: we replace Q(y) by the truncated virial expansion

$$Q(y)=1+\sum_{i=2}^{n}B_i y^{i-1} \tag{18}$$

where n will be appropriately choosen: n = 25. The corresponding free energy is then given by

$$Q(y)=\ln\rho+\sum_{i=2}^{n}\frac{B_i}{i-1}y^{i-1}-1 \tag{19}$$

Furthermore we expand the the lhs of (15) in a power series, which we denote by F (y):

$$F(y)=\sum F_i y^{i-1}$$

In the following we require that

$$F_i=0 \quad \text{for} \quad i=1,\ldots,n$$

Now k = 5 is set. We find that $F_1 = 0$ and that F_i for i > 1 depend not only on the six parameters αi, β in (14) but also on the virial coefficients. From

$$F_i=0 \quad \text{for} \quad i=2,\ldots,7$$

and setting $B_2 = 4$, $B_3 = 10$ and $B_4 = 18.3547...$ we obtain expressions for α_i and β as functions of B_5, B_6 and B_7. Inserting these in $F_i(i > 7)$ we get expressions of the form

$$F_8 = F_8(B_5, B_6, B_7, B_8),\ F_9 = F_9(B_5, B_6, B_7, B_8, B_9),\ldots$$

Here the F_i depend linearly on the B_i. Next we set

$$F_i=0 \quad \text{for} \quad i=8,\ldots,n$$

B_8 can be calculated from $F_8 = 0$, B_9 from $F_9 = 0$, and so on. All the $B_i(i > 7)$ thus depend on B_5, B_6 and B_7 which are considered as unknown quantities. To find the values of the latter, we make use of the requirement that the series (14) converges as rapidly as possible. This requirement can be expressed as follows:

$$|\alpha_5/\alpha_4| = \text{minimum} \tag{20}$$

At first sight we are confronted with a serious problem but it turns out that a simple solution can be found by means of an approximate equation of state which was derived earlier([5], appendix). This will be discussed in section 7.

7 An equation with one unknown parameter

In an earlier paper [5] the following equation of state was derived (the com-pressibility factor is denoted by $Q^*(y)$):

$$Q^*(y)=\frac{1+s_1y+s_2y^2+s_3y^3}{(1-y)^2(1+s_4y+s_5y^2)} \tag{21}$$

where

$$s5 = \frac{s_1 + s_2 + s_3 - 5}{6} - s_4 \tag{22}$$

These equations were derived on the basis of the expansion (12). In this derivation the term $A_0(y)$ canceled so that (13) could have been used as well. The thermodynamic condition was not taken into account. From (22) follows that the expression (21) contains four indepedent coefficients.

It is convenient to to expand $Q^*(y)$ in a power series:

$$Q^*(\mathrm{y}) = 1 + \sum_{\mathrm{i}=2}^{\mathrm{n}} B^* \mathrm{y}^{\mathrm{i}-1} \tag{23}$$

Here we set B_i^* =B_i for i = 2, ..., 5 where B_2, B_3 and B_4 are exactly known and B_5 is considered as an unknown quantity. It will turn out that the value of B_5 which follows from (21) is near to the numerically calculated value 28.2245 (see section 8). Moreover it can be shown that (N = B_4 − 16):

$$B_6^* = \left(3916 - 714B_4 + 51B_4^2 - B_4^3 - 84B_5 - 3B_4B_5 + 3B_5^2\right)/(3N) \tag{24}$$

and that

$$\begin{aligned} B_7^* = (&107848 + 15464B_4 - 606B_4^2 - 20B_4^3 + B_4^4 + 9860B_5 - 1464B_4B_5 \\ &+ 102B_4^2B_5 - 2B_4^3B_5 - 102B_5^2 - 6B_4B_5^2 + 3B_5^3)/\left(3N^2\right) \end{aligned} \tag{25}$$

All higher B_i^* depend on the value of B_5 which must be determined. For the coefficients s_i we found

$$s_1 = (-26 + 3B_4 - B_5)/N, \qquad s_2 = (148 - 17B_4 + B_4^2 - 6B_5)/(3N)$$

$$s_3 = (1334 - 151B_4 + 5B_4^2 - 9B_5)/(3N), \qquad s_4 = (6 + B_4 - B_5)/N$$

$$s_5 = (B_4 - 16)/3$$

$B_i = B_i^*$ for i > 5 implies that

$$B_6 = B_6^* \quad \text{and} \quad B_7 = B_7^*$$

As the accuracy of a computer is limited, these equations cannot be exactly fulfilled. Therefore we replace them by

$$B_6 = B_6^* \quad \text{and} \quad B_7 = B_7^*$$

where, in our case, $\in$ and $\in^*$ are of order 10^{-16}. In view of the smallness of this number the following question arises: may $\in$ and $\in^*$ be neglected or not? The answer is that they may not be neglected because if hypothetically $\in$ and $\in^*$ = 0 is set, the functions $f_i(y)$ diverge. Equation (15) can be solved as described in section 6, after having chosen a value of B_5 near 28 and making use of (24) and (25). The resulting virial expansions (18) and (23) then practically coincide so that both, and thus also equation (21), are almost exactly consistent with the thermodynamic condition. The above procedure is repeated with slightly different values of B_5 until the condition (20) is fulfilled. The result is

$$B_5 = 28.69, B_6 = 40.7369, B_7 = 54.3876$$

and

$$s_1 = 0.17097, s_2 = 0.130197 s_3 = -1.545818$$
$$s_4 = -1.82903, s_5 = 0.788256$$

Now we reconsider the expression (9) for the function $G_5(y)$. The calculations indicate that if $G_5(y)$ is replaced by any other function, the above results remain unchanged so that the derivation of (9) is superfluous. The reason is that $|/\alpha_5/\alpha_4|$ is very small (of order 10^{-13}) so that the term $\alpha_5 G_5(y)$ in (13) (with k = 5) may neglected. This could not be known beforehand. However, it should be remarked that (9) yields the smallest value of $|\alpha_5/\alpha_4|$.

Here the following question arises: are there values of B_5, B_6 and B_7 which yield smaller values of $|\alpha_5/\alpha_6|$? If this is the case then equation(21) is no longer valid. Numerical calculations indicate that the answer to this question is negative.

We thus may restrict ourselves to the case k = 4; it is easy to see that in this case $\in^*$ plays no role and that equation

(15), in the limit $\in \rightarrow 0$, leads to $Q(y) = -f_1(y)/f_2(y)$ where the terms $\ln y$ and $\ln(1-y)$ in (16) do not appear anymore and E drops out.

Before continuing we resume some recent (and also less recent) results of the research in the field of the virial coefficients.

8 A brief history of the virial coefficients

B_2 is easy to calculate (van der Waals). More difficult are the analytical calculations of B_3 and B_4. They were performed by Boltzmann at the end of the ninetienth century; the theory presented in [1] also yields B_3 and B_4.. Higher virial coefficients could not be calculated analytically. Only since the appearence of computers it was possible to determine B_i for $i > 4$ numerically, making use of the so called cluster expansions and Monte Carlo integration; for example: B_5 to B_{10} in [6,...,13]. Estimates of B_i for $i > 10$ were done by examining the simulation results, taking into account the values of B_2 to B_{10}. In this way Tian *et al* found values for B_{11} to B_{16} [14]; Hu and Yu: B_{11} to B_{18} [15]. Recently B_{11} was calculated numerically by Wheatley[16]; he obtained 127 ± 4. Schulz and Kofke[17] recalculated B_7 to B_{11}. For B_{11} they found 126.4 ± 0.6 which corresponds to the estimation 126.2 reported in[15]. More information about this subject can be found in the papers cited above and also in [18].

9 The virial coefficients

The approximate values of the virial coefficients yielded by the procedure de- scribed in sections 6 and 7 exhibit only small differences with those found in the literature as can be seen in table 1 and table 2 (the values are rounded).

— i	5	6	7	8	9	10	11
eqn.2	28.6	40.3	53.2	66.9	81.4	96.5	112
eqn.21	28.7	40.7	54.4	69.6	86.5	105	125
lit.[17]	28.2	39.8	53.3	68.5	85.8	106	126

Table 1

i	12	13	14	15	16	17	18
eqn.2	128	144	160	177	194	210	227
eqn.21	148	173	201	230	264	301	343
lit.[15]	149	174	202	231	262	295	330
lit.[14]	153	182	214	247	279		

Table 2

The uncertainty of B_5 is roughly estimated to be around 0.001; for the higher B_i the uncertainties increase with increasing i. For example: $B_{11} = 125.5 \pm 0.1$ and $B_{16} = 264 \pm 1$. The data in row 3 of table 1 are numerical results; B_{11} has the largest uncertainty: 126.4 ± 0.6 [17]. The data in row 3 and 4 of table 2 are estimates as pointed out in section 8; the second and the third digits are obviously uncertain, but the data of [15] seem to be more reliable than those of [14].

10 The compressibility factors

In the figure the compressibility factors yielded by equation (2) and by equations (18) or (21) are compared with the accurate results obtained by Speedy[19] who reported simulation values for $0.46 < y \leq 0.57$. As can be seen from the figure there are obvious deviations between two simulation points and the theoretical curve, namely at $y = 0.563$ and $y = 0.57$. Speedy argues that these points do not belong to the fluid branch but to a glassy branch (section 3 in [19]). Some of Speedy's results are summarized in table 3 and compared with the theoretical values. He reports that the uncertancies are of order 0.01. The values are depicted in the figure. In column 4 the corresponding values yielded by the semi-empirical equation of Carnahan-Starling are listed.

y	Speedy	eqn.2	eqn.21	CS
0.529	16.02	15.82	16.06	15.95
0.532	16.46	16.24	16.48	16.38
0.5369	19.90	1.66	16.92	16.82
0.5406	17.37	17.10	17.38	17.27

0.5443	17.91	17.55	17.85	17.75
0.5480	18.42	18.02	18.34	18.23
0.5554	19.55	19.00	19.37	19.26
0.5628	21.06	20.06	20.47	20.36
0.5700	22.40	21.15	21.61	21.50

Table 3

Here we should mention the more recent work of Kolafa *et al*[20]. They report simulated values of the compressibility factors up to y = 0.539. Their results coincide with those of Speedy but they are slightly more precise.

11 Summary

An approximate differential equation with the Helmholtz free energy and thus also the compressibility factor as unknown functions of the density was derived from the basic relations inclusive the thermodynamic condition. Although it was not possible to solve this equation exactly, the solution could be approxi- mated by a virial expansion with 25 terms. The resulting values of the virial coefficients are in good agreement with those found in the literature, provided that B_5, B_6 and B_7 are appropropriatly chosen. To find an appropriate choice we used an equation of state which was derived earlier; it contains only one parameter namely B_5. The latter could be determined by requiring that the series expansion (14) converges as rapidly as possible. The values of B_6 and B_7 then follow from (24) and (25). Numerical calculations indicate that (21) represents the optimal solution. The calculated compressibility factors repro- duce the simulation data slightly better than the old equation (2)

The author believes that the scaled particle theory cannot provide more inter- esting results with regard to the hard sphere fluid than those represented in this paper.

figure caption

vertical axis: compressibility factors

dots: some simulation data of Speedy

full line: eqn. (18) or (21)

dashed line: eqn. (2)

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